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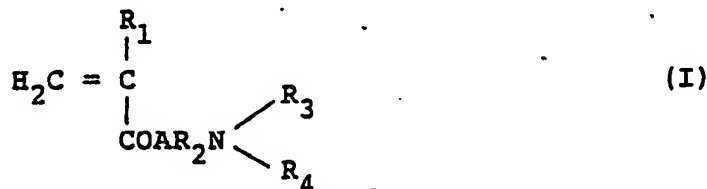
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(54) Hair-conditioning resin compositions.

(57) A hair conditioning resin composition comprises a copolymer resin modified with a zwitterionizing agent. The resin is prepared by copolymerizing in a hydrophilic solvent

(A) 65 - 90% by weight of vinyl monomer of formula (I):



wherein R₁ is H or Me, R₂ is Cl-4 alkylene, R₃ and R₄ are C₁₋₄ alkyl, and A is O or NH,

(B) 10 - 35% by weight of vinyl monomer of formula (II):

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wherein R_5 is H or Me and R_6 is C_{12-24} saturated or unsaturated alkyl, and

(C) 0 -25% by weight of other vinyl monomer. The zwitterionizing agent has the formula (III): XR_7COOB ... (III) wherein R_7 is C_{1-4} alkylene, X is Br, Cl or I, and B is an alkali metal ion, an ammonium salt or an amine salt.

HAIR-CONDITIONING RESIN COMPOSITIONS

This invention relates to novel hair-conditioning resin compositions having hair cosmetic properties such as softening, moderate moistening and wavsetting, and the ability to impart voluminousness and to facilitate combing out.

It has already been proposed to use quaternary ammonium salt compounds or quaternary ammonium salt-series polymers in hair-conditioning cosmetics, such as shampoos, rinses, hair treatments and wavsetting lotions, as disclosed in U.S. Patents 3,934,595, 4,030,512, 3,836,537 and 4,075,131; and in Japanese Patent Publication Nos. 11128/80 and 17009/80.

Among the known quaternary ammonium salt compounds are stearyl-trimethylammonium chloride, lauryl-trimethylammonium chloride and distearyl-dimethylammonium chloride. And among the known quaternary ammonium salt-series polymers are dimethylaminoethyl methacrylate-series quaternary ammonium salt polymers, diallyl-dimethylammonium chloride-series polymers and cationic celluloses.

The quaternary ammonium salt compounds have the double advantage of making the hair easier to comb and of softening it; however, they have the disadvantages of reducing the voluminousness of the hair and settlement of the hair, and of making it more difficult to set. The quaternary ammonium salt-series polymers have the advantage of making the hair easier to comb; however, they have the disadvantage of imparting a specific

malaise to the hair, that is, the accumulation of the polymers on the hair by the repetitious use thereof, known as the build-up problem, impairs the good feeling of the hair. Furthermore, these quaternary ammonium salt compounds and polymers have other disadvantages in their incompatibility with anion-charged compounds caused by their cationic charge and the hyperhygroscopicity of the quaternary ammonium salt group; in the feel of the hair at high temperature and humidity; in the worsening of the hair's condition; and in the rapid losing of the hair's wavsetting property.

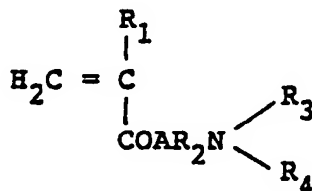
On the other hand, although being useful for setting the hair, the zwitterionic polymers according to the prior art are not useful for conditioning hair.

It is therefore an object to eliminate or reduce the disadvantages of the prior art preparations.

We have found that certain zwitterionic copolymers exhibit an excellent hair-conditioning effect.

According to the present invention there is provided a hair-conditioning resin composition prepared by modifying a copolymer resin with a zwitterionizing agent, said copolymer resin being prepared by copolymerizing in a hydrophilic solvent a polymerizable mixture containing

(A) 65 -90% by weight of a polymerizable vinyl monomer having the following general formula (I):

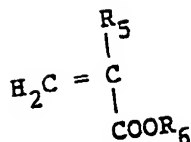


(I)

wherein R₁ represents a hydrogen atom or a methyl group, R₂ represents an alkylene group having from 1 to 4 carbon atoms, R₃ and R₄ each represents an alkyl group having from 1 to 4 carbon atoms, and A repre-

sents an oxygen atom or an NH group.

(B) 10 -35% by weight of polymerizable vinyl monomer having the following general formula (II):



wherein R_5 represents a hydrogen atom or a methyl group, and R_6 represents a saturated or unsaturated alkyl group having from 12 to 24 carbon atoms, and

(C) 0 -25% by weight of other polymerizable vinyl monomer, said zwitterionizing agent having the following general formula (III) $\text{XR}_7\text{COOB} \dots$ (III) wherein R_7 represents an alkylene group having from 1 to 4 carbon atoms, X represents a bromine, chlorine or iodine atom, and B represents an alkali metal ion, an ammonium salt or an amine salt.

On occasion, the preparation of the resin composition of the invention preferably includes the final steps of filtering any precipitate, and purifying with ion-exchange resin.

Monomer (A) is a derivative of acrylic acid or methacrylic acid represented by the above-mentioned general formula (I). Hereinafter, both the acrylic acid and methacrylic acid are generally referred to as "(meth)acrylic acid". In the above formulae (I) to (III), R_1 , R_2 , A and B represent substituents as defined above, and particularly, it is preferred that R_1 is a methyl group, R_2 is an alkyl group having 2 to 3 carbon atoms, R_3 and R_4 are each a methyl group or an ethyl group, and A is an oxygen atom. Examples of preferred Monomer (A) include dimethylamino-ethyl (meth)acrylate, dimethylamino-propyl (meth)acrylate, diethylamino-ethyl (meth)acrylate, dimethylamino-ethyl (meth)acrylamide and diethylaminopropyl (meth)acrylamide.

The proportion of Monomer (A) to the total monomer content is 65 -90% by weight, and preferably, 70 -85% by weight. If the proportion is less than 65% by weight, the resulting zwitterionic copolymer films are hard, thereby making the hair stiff and more difficult to comb, and reducing its moisture content. If the proportion exceeds 90% by weight, the resulting copolymer films are tacky, thereby making the hair heavy, reducing its voluminousness and impairing its ability to settle.

(II)

Monomer (B) is a (meth)acrylic ester represented by the above general formula (II), in which it is generally preferred that R_5 is a methyl group and R_6 is an alkyl group having from 16 to 20 carbon atoms.

If R_6 is an alkyl group having less than 12 carbon atoms, the resulting zwitterionic copolymer films are hard, thereby making the hair stiff and more difficult to comb, and reducing its moisture content. Examples of Monomer (B) include palmityl (meth)acrylate, stearyl (meth)acrylate, oleyl (meth)acrylate, myristyl (meth)acrylate and behenyl (meth)acrylate.

The proportion of Monomer (B) to the total monomer content is 10 -35% by weight, and preferably, 15 -30% by weight. If the proportion is less than 10% by weight, the resulting copolymer films are tacky, thereby making the hair heavy and losing its voluminousness and settlement ability. If the proportion exceeds 35% by weight, the resulting copolymer films are hard, thereby making the hair stiff and more difficult to comb, and imparting thereto the above-mentioned malaise.

Other vinyl monomer may be added as component (C) to Monomers (A) and (B) in order to give moderate hardness and flexibility to the resulting films as necessary. Examples of the other vinyl monomer include methyl (meth)acrylate, isobutyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, acrylonitrile, acrylamide, styrene, vinyl acetate, hydroxyethyl (meth)acrylate, (meth)acrylic ester of polyethylene glycol or polypropylene glycol and N-vinyl-pyrrolidone. The proportion of the other vinyl monomer to the total monomer content is 0 -25% by weight.

Specific examples of the zwitterionizing agent represented by the above-mentioned general formula (III) include sodium monobromoacetate, potassium monochloroacetate, lithium monochloropropionate, neutral matter of monochloroacetic acid and ammonia, 2-amino-2-methyl-1-propanol, triethanolamine and 2-amino-2-ethyl-1,3-propanediol.

The proportion of the zwitterionizing agent to Monomer (A) (or to the total of Monomer (A) and other Monomer (C) in the case that the other monomer component (C) contains nitrogen atoms to be zwitterionized) is 0.7 -1.3, preferably 0.8 -1.2, mol per mol of Monomer (A) or Monomer (A) and (C).

The above-mentioned Monomers (A), (B) and (C) are copolymerized in a hydrophilic solvent. The term "hydrophilic solvent" used herein means an organic solvent having a solubility of 10 [g/100 g water/25°C] or more in water. Preferred examples of the hydrophilic organic solvent used in the present invention include methanol, ethanol, isopropanol, ethylene glycol, ethylcellosolve, dioxane, methyl acetate and dimethylformamide. The hydrophilic organic solvent may be in the hydrous state as long as no trouble is thereby incurred during polymerization, filtration and the like. An example of hydrous organic solvent is 95% ethanol.

Copolymerization is carried out by a conventional solution polymerization method, for example one comprising the steps of dissolving the monomers in the solvent, adding an initiator thereto, and heating the mixture with stirring under nitrogen stream. Preferred examples of the initiator include peroxides, such as benzoyl peroxide, a lauroyl peroxide and azo compounds, such as azo-bis-isobutyronitrile.

The copolymerization may be carried out simultaneously or partially and progressively with respect to all the kinds and amounts of monomers.

It is preferred that the solvent is used in an amount such that the concentration of the resulting copolymer solution lies within the range from about 30 to about 70% by weight.

The polymerization conditions, such as the method of introducing the monomers and initiator, and the amount of the solvent used, are suitably selected. It is, however, preferred that the conditions are determined so that the resulting copolymer has a numerical average molecular weight of from 30,000 to 500,000.

The zwitterionizing reaction can be carried out by adding a hydrophilic solvent solution or suspension of the zwitterionizing agent completely or partially to the copolymer solution after the polymerization, and heating at a temperature of from about 70 to about 80°C for a time of from about 4 to about 12 hours with suitable stirring in an inactive atmosphere, for example, in a flow of nitrogen gas.

Where B in the general formula (III) is an alkali metal such as sodium, potassium or lithium, an inorganic salt (BX) is precipitated with the progression of the zwitterionizing reaction; the precipitated

inorganic salt is removed. Removal of the precipitated inorganic salt is performed by any solid-liquid separation method such as centrifugal separation or filtration.

The zwitterionized copolymer solution obtained by such methods of removing the inorganic salt may still contain a little (about 0.1 -about 1% by weight) of inorganic salt. To remove such a small remaining amount of inorganic salt, the zwitterionized copolymer solution can be treated by batch-type or flow-type ion exchange. Thereby, the inorganic salt content can be reduced to a value of 0.1% by weight or less.

Where B in the general formula (III) is an amine or an ammonium salt, an organic salt (BX) is not precipitated with the progression of the zwitterionizing reaction. Accordingly, the zwitterionized polymer solution can be directly used as a homogeneous solution without the steps of separating and removing BX.

The thus obtained resin can be used, in the form of a hydrophilic solvent solution, of a solution from which the solvent has been removed or of a solution in which the hydrophilic solvent has been replaced by pure water, in cosmetics for hair.

The resin according to the present invention is compatible with and may be added to a hair cosmetic such as a shampoo, rinse, hair treatment or wavesetting lotion, in order to give hair conditioning effects. The proportion of the resin to the cosmetic ranges from 0.01 to 5% by weight as zwitterionic polymer.

The present invention will now be illustrated in more detail in the following Examples thereof.

EXAMPLE 1

70 parts by weight of dimethylamino-ethyl methacrylate, 10 parts by weight of myristyl methacrylate, 20 parts by weight of stearyl methacrylate, and 50 parts by weight of ethanol were introduced into a five neck polymerization flask, equipped with a reflux cooler, a dropping funnel, a thermometer, a glass inlet for nitrogen substitution, and a stirrer. 0.6 part by weight of α,α' -azo-bis-isobutyronitrile was added thereto and the mixture was refluxed with heating at 80°C in a flow of nitrogen gas for 4 hours to thus carry out copolymerization.

At the end of the copolymerization, an ethanol suspension containing 40% by weight of potassium monochloroacetate equimolar with the dimethylamino-ethyl methacrylate was added to the

flask, drop by drop, by means of the dropping funnel. The mixture was heated at 80°C in a flow of nitrogen gas for 10 hours to carry out the zwitterionizing reaction.

A precipitate was separated from the obtained viscous suspension by the use of a pressure filter - (made by Nippon Dying Machine Mfg. Co., Ltd.).

The filtrate was passed through a column filled with recovered cation-exchange resin (tradename "DIAION PK-220"; in which, after recovery the system was subject to substitution of ethanol) and then passed through a column filled with recovered anion-exchange resin (tradename "DIAION PA-418"; in which, after recovery the system was subject to substitution of ethanol) to thus carry out purification.

The thus obtained light-yellow transparent solution was diluted with ethanol so as to adjust the copolymer resin content thereof to 30% by weight.

The thus obtained copolymer resin solution was subject to measurement of numerical average molecular weight by an osmotic pressure method - (at 25°C) by using an osmometer (made by Parkin-Elmer Inc.), and the resultant numerical average molecular weight was 300,000.

The resin ethanol solution was diluted 60 times with pure water. The diluted solution was applied to a 23 cm long and 2 g weight bundle of hair. The hair was then dried with exposure to air. The hair-conditioning effect of the solution was excellent. (See Table 1.)

Next, 3 g of the resin ethanol solution were introduced to 100 g of an aqueous solution containing 20% by weight of alcohol sulfate sodium salt to thus obtain a shampoo liquid. The shampoo liquid was applied to a 23 cm long and 2 g weight bundle of hair. The hair was then washed with water and dried with exposure to air. The hair-conditioning effect of the liquid was excellent. (See Table 1.)

EXAMPLES 2-4

Resin solutions were prepared in the same manner as described in Example 1 except that the monomers used in Example 1 were replaced by monomers shown in Table 1. The resulting resin solutions were then evaluated in the same manner described in Example 1. The hair-conditioning effect of the respective solution was excellent. (See Table 1.)

EXAMPLE 5

Copolymerization was carried out in the same manner as described in Example 1 except that the monomers used in Example 1 were replaced by monomers shown in Table 1. At the end of the copolymerization, an ethanol suspension containing 40% by weight of neutral matter of monochloroacetic acid and 2-amino-2-methyl-1-propanol equimolar with the dimethylamino-ethyl methacrylate was added to the polymerization flask, drop by drop, by means of the dropping funnel. The mixture was heated at 80°C for 8 hours to thus carry out the zwitterionizing reaction.

The thus obtained solution was diluted with ethanol so as to adjust the resin content thereof to 30% by weight. The resulting resin solution was then evaluated in the same manner as described in Example 1. The hair-conditioning effect of the solution was excellent. (See Table 1.)

EXAMPLE 6

A resin solution was prepared in the same manner as described in Example 5 except that the monomers used in Example 5 were replaced by monomers shown in Table 1 and the zwitterionizing agent was replaced by neutral matter of monochloroacetic acid and triethanolamine. The resulting resin solution was then evaluated in the same manner as described in Example 1. (See Table 1.)

COMPARATIVE EXAMPLES 1-4

Resin solutions were prepared in the same manner described in Example 1 except that the monomers used in Example 1 were replaced by monomers shown in Table 2. The resulting resin solutions were then evaluated in the same manner as described in Example 1. The resin solutions were inferior in stiffness, combing-out, and so on, that is, they were unsatisfactory as hair-conditioning resins. (See Table 2.)

COMPARATIVE EXAMPLE 5

A resin solution was prepared in the same manner as described in Example 1 except that the ethanol used for the polymerization was used in the amount of 150 parts by weight. The resulting resin solution was then evaluated in the same manner as described in Example 1. The resin solution was inferior in tackiness, combing-out, and so on, that is, it was unsatisfactory as hair-conditioning resin. - (See Table 2.)

Measurement of molecular weight was made on the copolymer resin in the same manner as described in Example 1. The resin had a numerical average molecular weight of 20,000.

COMPARATIVE EXAMPLE 6

70 parts by weight of dimethylamino-ethyl methacrylate, 10 parts by weight of myristyl methacrylate, 20 parts by weight of stearyl methacrylate, and 45 parts by weight of ethanol were introduced into the same flask as described in Example 1 and heated to 70°C in a flow of nitrogen gas. A solution obtained by dissolving 0.3 part by weight of α,α' -azo-bis-isobutyronitrile into 5 parts by weight of ethanol was added to the flask having been heated to 70°C, drop by drop, for 4 hours. After the dropwise addition, the temperature was maintained at 70°C for 3 hours to thus obtain a copolymer. After the end of the zwitterionization, the process performed in Example 1 was followed.

The resulting resin solution was then evaluated in the same manner as described in Example 1. The resin solution was inferior in combing-out and stiffness, that is, it was unsatisfactory as hair-conditioning resin. (See Table 2.)

Measurement of molecular weight was made on the copolymer resin in the same manner as described in Example 1. The resin had a numerical average molecular weight of 600,000.

The performance of the respective resin shown in Tables 1 and 2 was evaluated with organoleptic test and the types thereof were classified into the following three.

o : Good

Δ : Unsatisfactory

x : Very bad

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TABLE 1

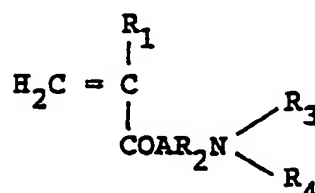
Composition (s by weight)				Performance								
Example	Monomers (A)	Monomers (B)	Other Monomers (C)	Pure water Dilution			Shampoo - Model					
				Volumi- nousness	Stiff- ness	Comb- out	Tacki- ness	Volumi- nousness	Stiff- ness	Comb- out	Tacki- ness	
1	Dimethylamino-ethyl methacrylate	70 Myristyl methacrylate	10	o	o	o	o	o	o	o	o	o
		Stearyl methacrylate	20									
2	Diethylamino-ethyl methacrylate	85 Behenyl methacrylate	15	o	o	o	A	A	o	o	o	o
3	Dimethylamino-propyl acrylamide	70 Stearyl methacrylate	30	o	o	o	o	o	o	o	o	o
4	Dimethylamino-ethyl methacrylate	65 Stearyl methacrylate	20 Polypropylene 15 glycol (n=9) methacrylic acid ester	o	A	o	o	o	o	o	o	o
5	Dimethylamino-ethyl methacrylate	70 Stearyl methacrylate	20	o	o	o	o	o	o	o	o	o
		Stearyl acrylate	10									
6	Dimethylamino-propyl methacrylate	75 Behenyl methacrylate	15 Butyl methacrylate	10	o	o	o	o	o	o	o	o

TABLE 2

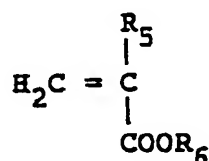
Comp. Example	Composition (% by weight)				Performance							
	Monomers (A)	Monomers (B)	Other Monomers (C)		Pure water Dilution				Shampoo - Model			
					Volumi- nousness	Stiff- ness	Combing- out	Tacki- ness	Volumi- nousness	Stiff- ness	Combing- out	Tacki- ness
1	Diethylamino-ethyl methacrylate	60 Myristyl methacrylate	20 Lauryl methacrylate		o	Δ	Δ	Δ	o	o	Δ	Δ
2	Dimethylamino-ethyl methacrylate	50		Methyl methacrylate	25	o	x	x	o	x	x	o
				Isobutyl methacrylate	25							
3	Dimethylamino-propyl methacrylate	50 Tridecyl methacrylate	30	Ethyl methacrylate	20	o	x	x	o	x	x	o
4	Dimethylamino-ethyl methacrylate	40 Stearyl methacrylate	20	Polypropylene glycol (n-9) methacrylic acid ester	20	o	x	x	o	x	x	o
				Methyl methacrylate	20							
5	Dimethylamino-ethyl methacrylate	70 Myristyl methacrylate	10		x	o	Δ	Δ	x	o	Δ	Δ
				Stearyl methacrylate	20							
6	Dimethylamino-ethyl methacrylate	70 Myristyl methacrylate	10		o	x	x	x	o	Δ	x	o
				Stearyl methacrylate	20							

Claims

1. A hair-conditioning resin composition prepared by modifying a copolymer resin with a zwitterionizing agent, characterised in that said copolymer



wherein R_1 represents a hydrogen atom or a methyl group, R_2 represents an alkylene group having from 1 to 4 carbon atoms, R_3 and R_4 each represent an alkyl group having from 1 to 4 carbon atoms, and A represents an oxygen atom



wherein R_5 represents a hydrogen atom or a methyl group, and R_6 represents a saturated or unsaturated alkyl group having from 12 to 24 carbon atoms, and

(C) 0 -25% by weight of other polymerizable vinyl monomer, and in that said zwitterionizing agent has the following general formula (III): XR_7COOB ... (III) wherein R_7 represents an alkylene group having from 1 to 4 carbon atoms, X represents a bromine, chlorine or iodine atom, and B represents an alkali metal ion, an ammonium salt or an amine salt.

2. A composition as claimed in claim 1, in which said resin has a numerical average molecular weight of from 30,000 to 500,000.

3. A composition as claimed in claim 1 or 2, in which in the general formula (I) R_1 represents a methyl group, R_2 an alkyl group having 2 or 3 carbon atoms, R_3 and R_4 a methyl or ethyl group, and A an oxygen atom.

resin is prepared by copolymerizing in a hydrophilic solvent a polymerizable mixture containing

(A) 65 -90% by weight of a polymerizable vinyl monomer having the following general formula - (I):

(I)

or an NH group,

(B) 10 -35% by weight of polymerizable vinyl monomer having the following general formula - (II):

(II)

4. A composition as claimed in claim 1 or 2, in which said monomer (A) is selected from dimethylamino-ethyl methacrylate, diethylamino-ethyl methacrylate, dimethylamino-propyl acrylamide and dimethylamino-propyl methacrylate.

5. A composition as claimed in any preceding claim, in which in the general formula (II) R_5 is a methyl group and R_6 an alkyl group having from 16 to 20 carbon atoms.

6. A composition as claimed in any one of claims 1 to 4, in which said monomer (B) is selected from myristyl methacrylate, stearyl methacrylate, behenyl methacrylate, and stearyl acrylate.

7. A composition as claimed in any preceding claim, in which said zwitterionizing agent is selected from potassium monochloroacetate, neutral matter of monochloroacetic acid and 2-amino-2-methyl-1-propanol, and neutral matter of monochloroacetic acid and triethanolamine.